Age Dating Groundwater

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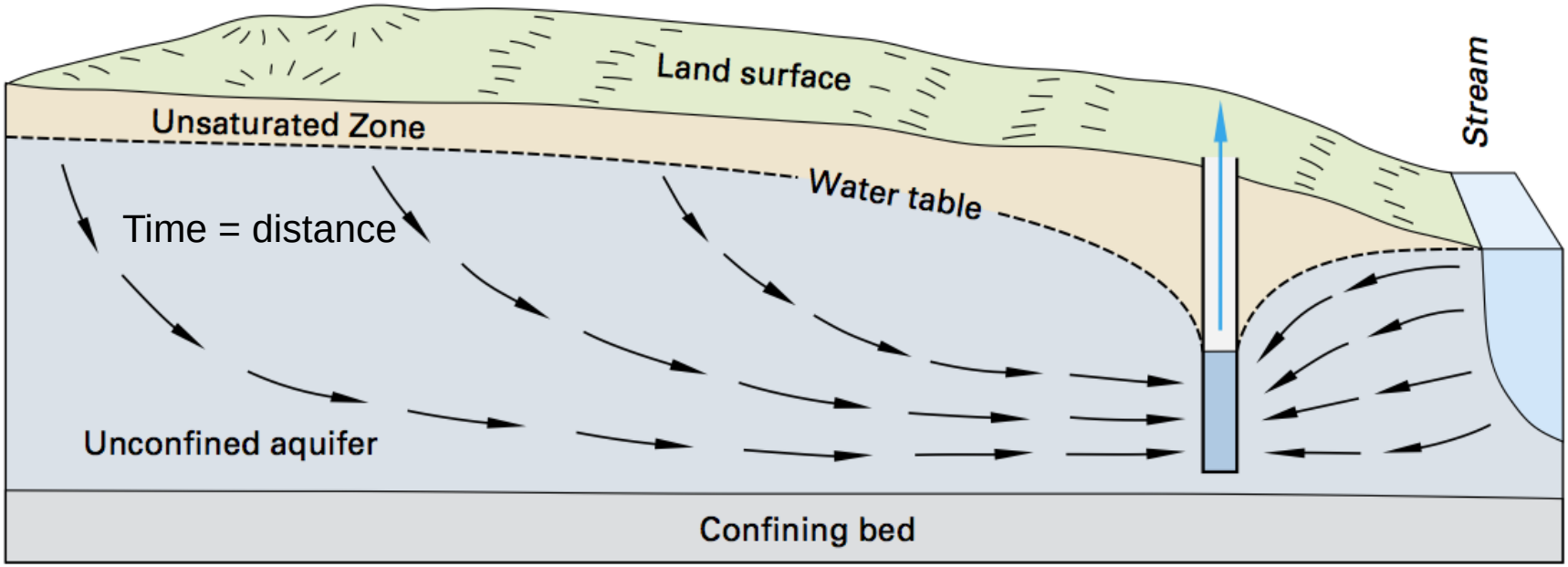
Age-Dating Groundwater: Talk Outline

- **Introduction**
  - What is groundwater age?
  - Why would anyone want to know groundwater age?
  - How do you determine groundwater age?

- **INTRODUCED NOBLE GAS TRACERS:**
  Groundwater age dating for young water (0-2 years) using an added tracer.
  - *Application*: Recycled wastewater reuse; Managed aquifer recharge
  - *Opportunity*: Commercialize LLNL NG-MIMS

- **TRITIUM/HELIUM-3 AGE DATING:**
  Groundwater age dating for older water (2-50 years) using intrinsic tracers
  - *Application:* Contaminant attribution; Groundwater monitoring; Basin characterization
  - *Opportunity*: Make method more available to California water community

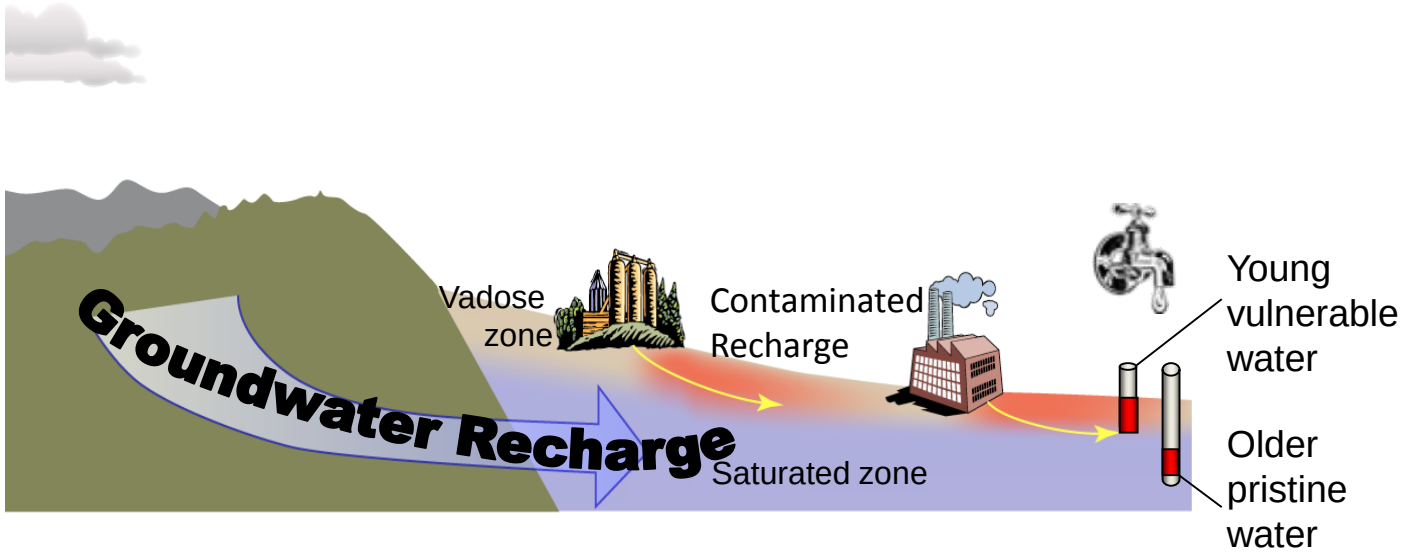
What is groundwater age?



Groundwater age is the travel time between recharge and discharge.

Groundwater age usually refers to the residence time of water in the subsurface between its isolation from the atmosphere just below the water table to its discharge to a well, spring, river, lake or ocean.

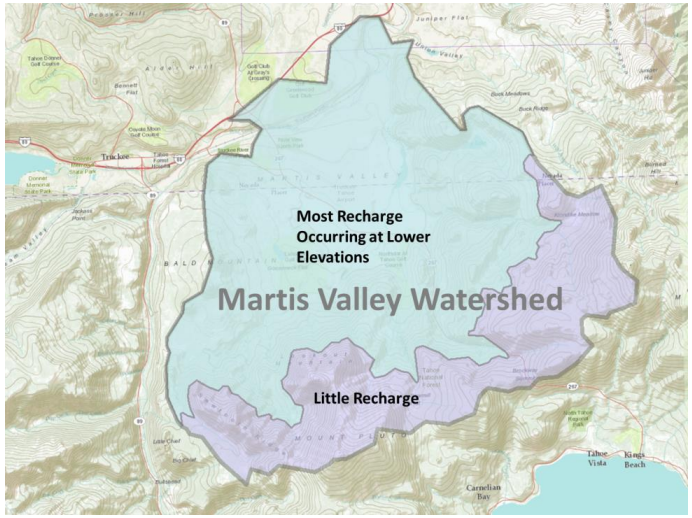
Why would you want to determine groundwater age?

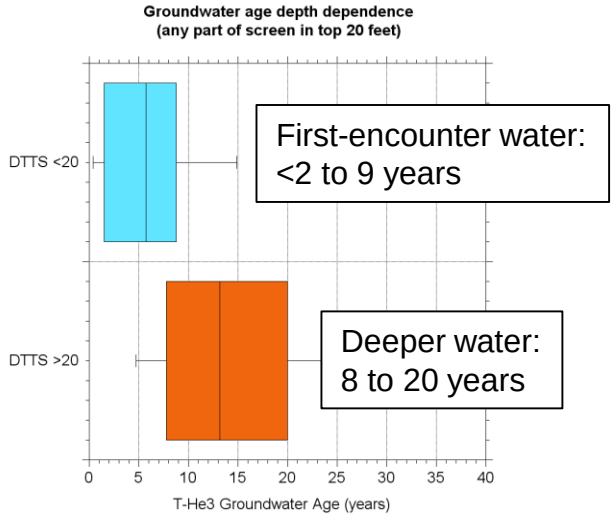


Groundwater age dating can provide valuable constraints on **when and where groundwater was recharged**, and on the **age and source of groundwater contaminants**.

Why would you want to determine groundwater age?

- **Vulnerability assessment**
  - Rapid survey of vulnerability: young = vulnerable
    (When will MTBE or nitrate show up in my well?)
- **Basin characterization**
  - Sustainable use or groundwater mining?
  - What are suitable areas for managed aquifer recharge
- **Contaminant attribution**
  - Is the contamination from legacy or current source?
    (Old irrigated agriculture or new residential septic?)
  - Is the contamination from local or non-local sources?
- **Groundwater monitoring**
  - Regional monitoring of dairies and irrigated lands
  - Assessment of best management practices
- **Regulatory compliance:**
  managed aquifer recharge of recycled water
  - Retention time regulations for drinking water wells.





How do you determine groundwater age?

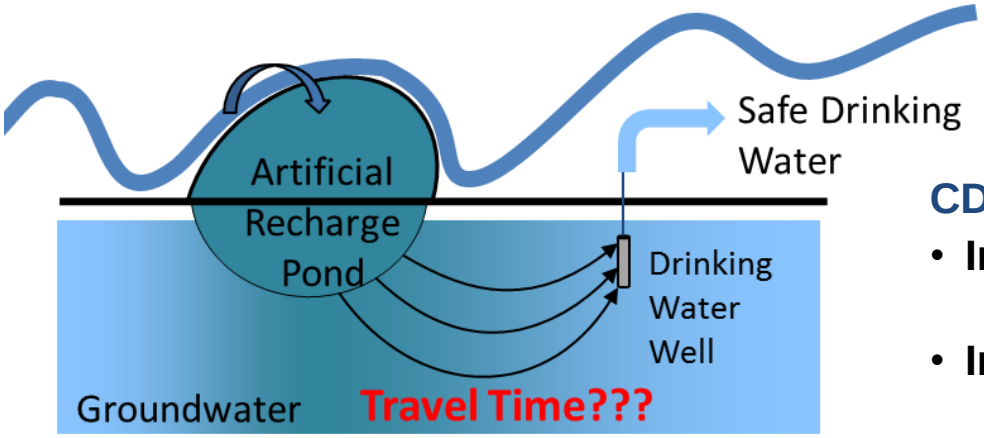
Recharge of treated wastewater requires a subsurface residence time of six months to achieve a 6-log reduction in pathogens.

Method	General accuracy	General level of effort	Retention time (months)	Safety factor
Formula (Darcy's)	Poor	Some info on aquifer	24	4.0
3-D model	Fair	Lot of info on aquifer	12	2.0
Intrinsic tracer	Better	Sampling of existing tracers	9	1.5
Added tracer	Desired	Track added tracer	6	1.0

California Department of Public Health, 2008. Draft Groundwater Recharge Reuse Regulations (Title 22, California Code of Regulations; Division 4,. Environmental Health; Chapter 3. Recycling Criteria).

Managed aquifer recharge of recycled wastewater requires tracing groundwater on a 0-2 year time scale.

Age tracers for short travel times (0-2 years):
Managed aquifer recharge



1 month = 1 log removal

The use of treated wastewater used for groundwater recharge requires demonstrating a subsurface residence time of months to years.

CDHS guidelines for 6-log removal credit

- **Intrinsic Tracer***: Sample existing tracers*.
  Demonstrate a retention time of **9 months**
- **Introduced Tracer:** *Track an added tracer.*
  Demonstrate a retention time of **6 months**

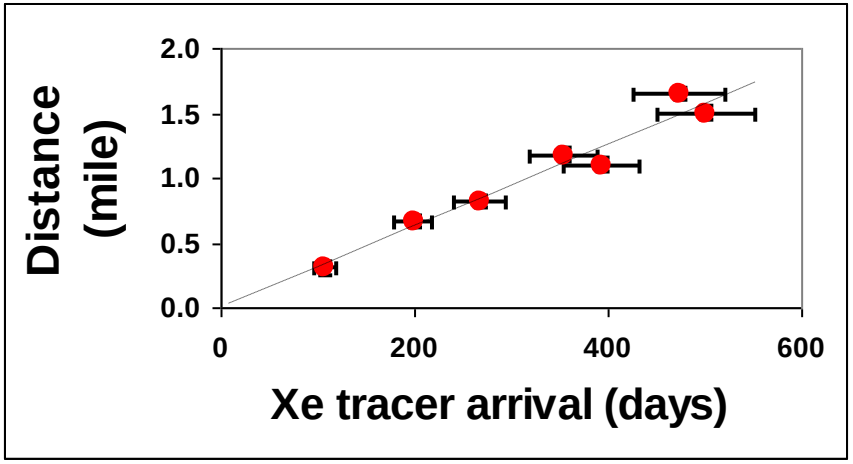
Current tracers

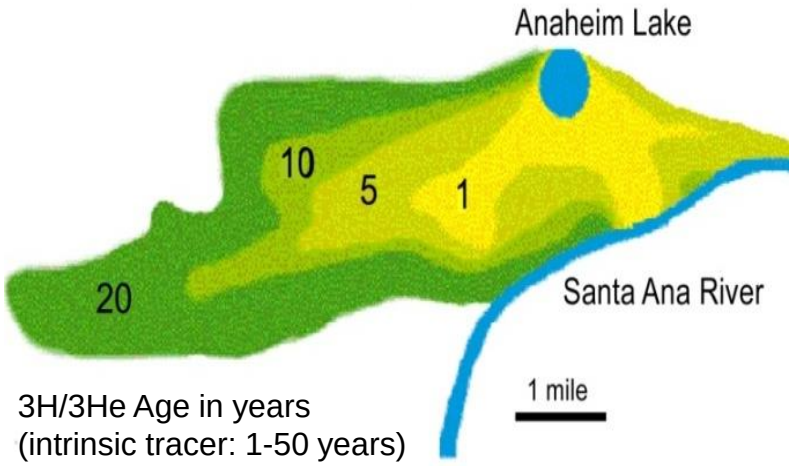
- **Intrinsic: Tritium/helium-3**
  Cannot determine ages <1-2 years
- **Introduced: Sulfur hexafluoride (SF6):**
  Greenhouse gas; being phased out by CARB
- **Introduced: Isotopic noble gases:**
  Limited and expensive analysis,
  Specialized sampling

The old approach: Introduced isotopically-enriched noble gas tracers analyzed at LLNL by Noble Gas Mass Spectrometry in a dedicated facility

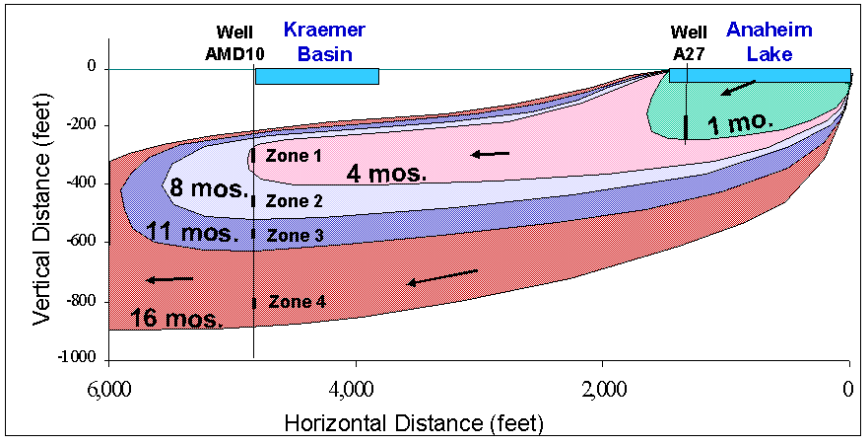
Noble gases meet the technical specs for managed aquifer recharge tracers

- They are non-reactive in aqueous systems.
- They are non-toxic and approved for potable systems.
- They can be measured in small samples (10 mL).
- Multiple tracers can be introduced at different times or to places and be measured in a single analysis.
- They are widely available and are inexpensive enough (~1$/1000 m^3) for large-scale experiments .





3H/3He Age in years
(intrinsic tracer: 1-50 years)

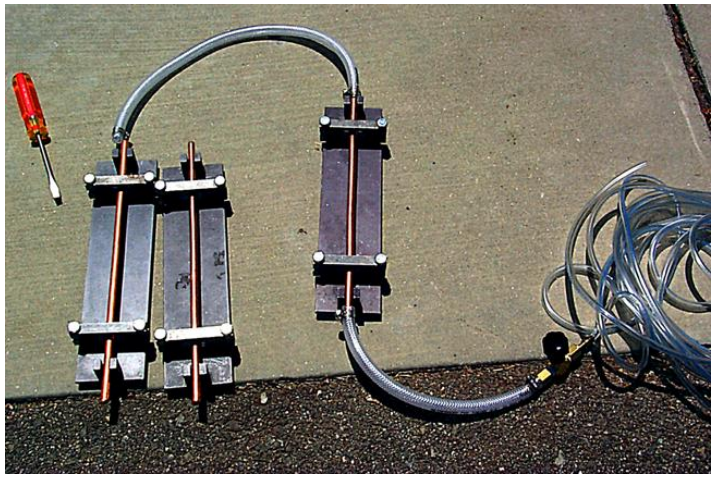


Clark J. F., Hudson G. B., Davisson M. L., Woodside G., and Herndon R. (2004) **Geochemical imaging of flow near an artificial recharge facility, Orange County, California.** ***Ground Water 42(2), 167-174.***

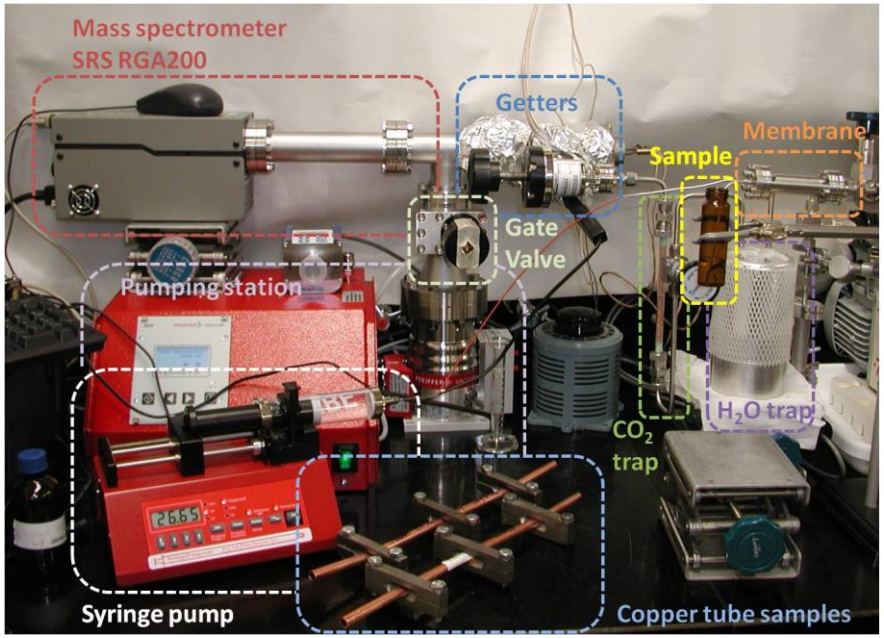
The old approach: Introduced isotopically-enriched noble gas tracers analyzed at LLNL by Noble Gas Mass Spectrometry in a dedicated facility

Limitations of the old method

- Inefficient tracer introduction:
  Significant loss of gas from bubbling
- Specialized sampling protocols: *Copper tubes*
- Low-throughput: *8 samples/day*
- Near-unique facility:
  LLNL, ~$1M setup and highly trained staff
- No possibility for field deployment
- Low possibility for commercialization

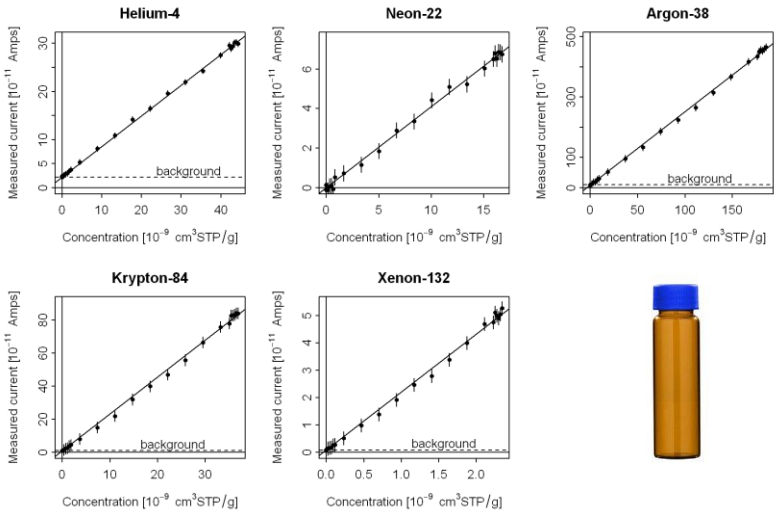


The new approach: Introduced noble gas tracers analyzed on a small, simple Noble Gas Membrane Inlet Mass Spectrometer (NG-MIMS)



The new method addresses these limitations

- Efficient tracer introduction:
  Diffusion tubing for <5% loss
- Standard sampling protocols: *40-mL VOA vial*
- High-through: *8-10 samples/hour*
- Benchtop instrument:
  <$50K in commercal off-the-shelf components
- Strong possibility for field deployment
- Strong possibility for commercialization



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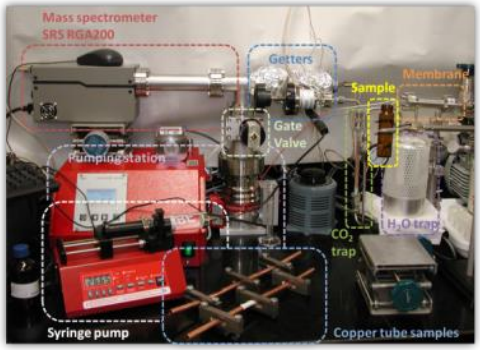
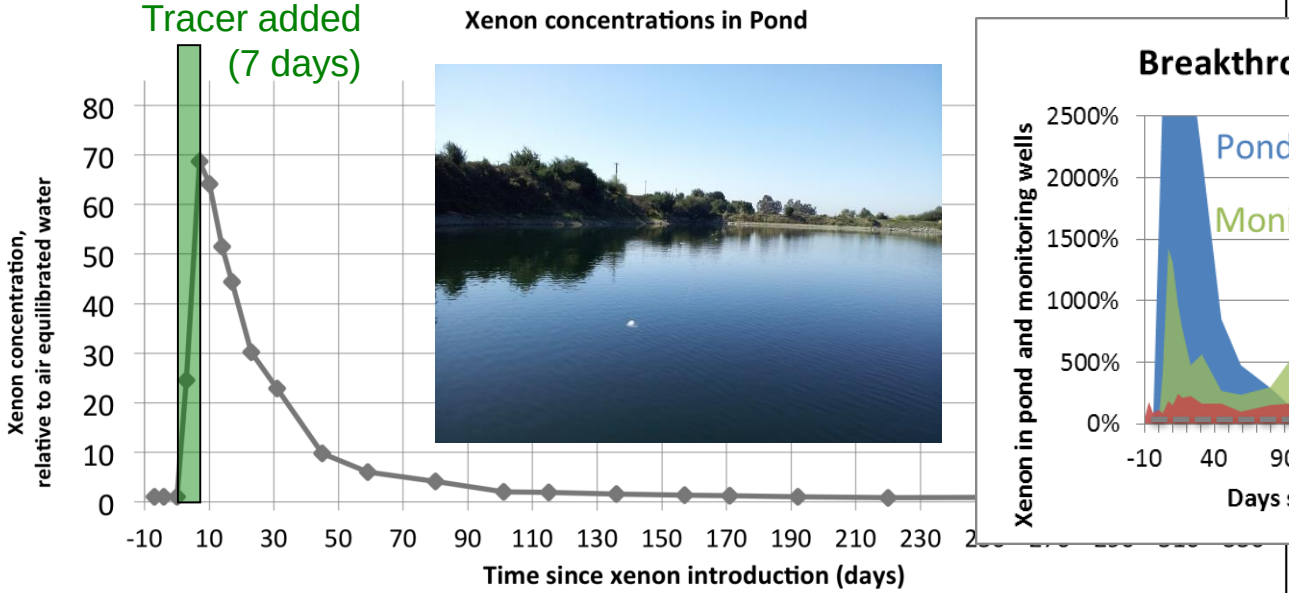
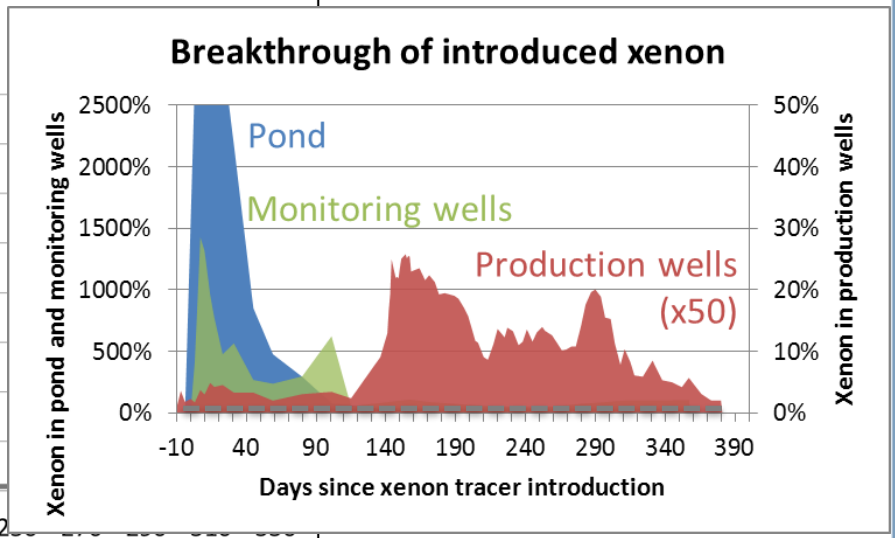


*Fast analyses on a new **NG-MIMS** bench-top instrument made with commercial parts*

THE NEW APPROACH HAS BEEN FIELD TESTED.

- **The new approach is inexpensive:**
  Xenon tracer studies at a similar cost to SF6,
- **Tracer introduction and sample collection are simple:**
  Un-attended introduction at near 100% efficiency
  Sample collection using standard methods
- **The new approach is sensitive:**
  A small fraction (0.1%) of surface recharge water can be detected in drinking water production wells





NG-MIMS (Introduced xenon tracer analysis): Opportunities

- **Add groundwater xenon tracing to your bag of tools**
  - LLNL does all sample processing, analysis and data reduction
  - LLNL provides guidance on dosing and sampling
  - LLNL provides or assists with data interpretation

- **Contract with LLNL directly or indirectly**
  - Work with an analytical service provider that contracts with LLNL:
    - *Standard contract quickly put in place*
    - *LLNL has a non-exclusive contract with Hydrotrace, LLC*
  - Contract directly with LLNL:
    - *Lengthier process, non-standard contract*
    - *Act as an analytical services provider of this capability to the California water resource community*

NG-MIMS (Introduced xenon tracer analysis): Opportunities

- **Contract with LLNL to build an instrument or to lease an instrument for an extended tracer campaign**
  - We are currently developing a contract with a non-California utility with this concept

- **Use the LLNL design to build and sell a commercial instrument**
  - LLNL has an ROI but not a patent
  - There is a lot of room for improvement
    - Place instrument in a standard cabinet
    - Ruggedize for field deployment
    - Develop software
      - Integrate instrument control and data acquisition
      - Develop a data reduction module
      - Make more use friendly

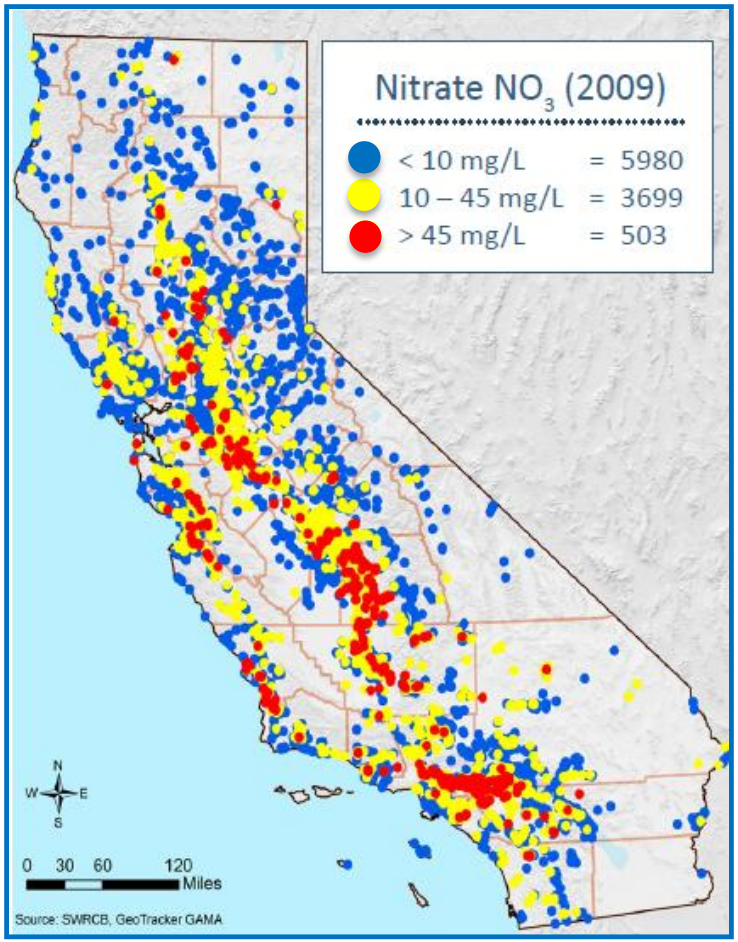
NG-MIMS (Introduced xenon tracer analysis): Intellectual Property

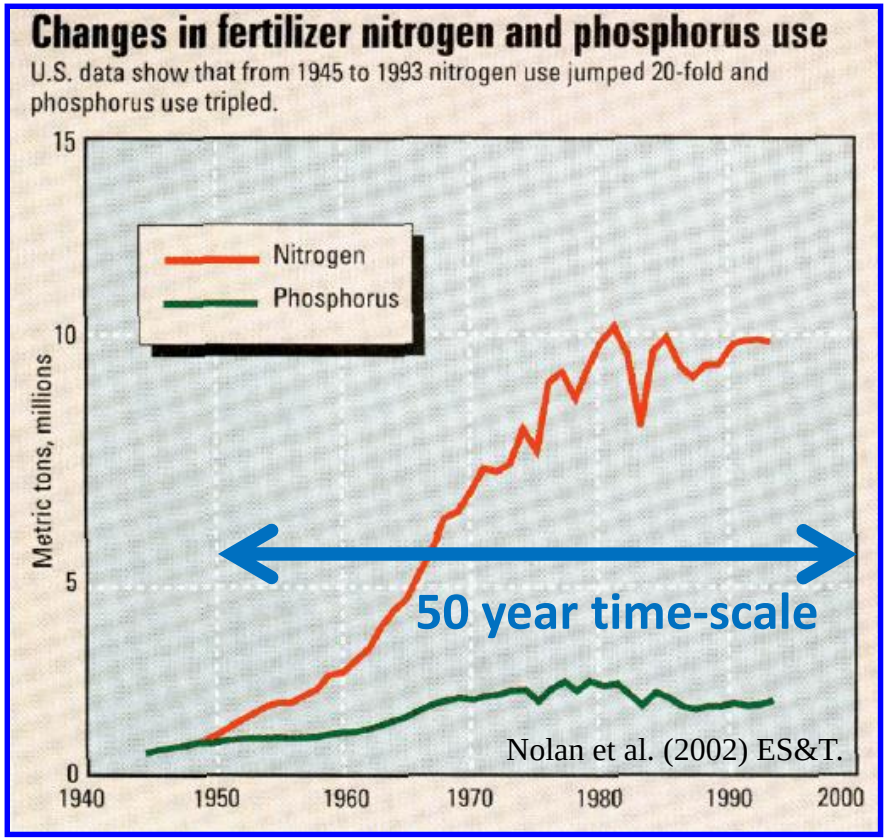
- **LLNL does have a record of invention in NG-MIMS**
  - M. Singleton and A. Visser, 2010, Noble Gas Membrane Mass Spectrometer, IL-12385
  - LLNL has elected not to pursue a patent at this time

- **LLNL does have reports and an accepted peer-reviewed publication**
  - **Method report :** Visser, A., Singleton, M., Hillegonds, D., Velsko, C., Moran, J.E., Esser, B.K., 2012. California GAMA Special Study: A Noble Gas Membrane Inlet Mass Spectrometry (NG-MIMS) system for water and gas samples. Lawrence Livermore National Laboratory LLNL-TR-548931, p. 22.
  - **Field study report:** Visser, A., Singleton, M., Hillegonds, D., Velsko, C., Moran, J.E., Esser, B.K., 2013. California GAMA Special Study: Rapid, Low-Cost Noble Gas Tracer Monitoring to Determine Travel Times at Recharge Operations. Lawrence Livermore National Laboratory LLNL-TR-534291, p. 40.
  - **In press manuscript:** Visser, A., Singleton, M.J., Hillegonds, D.J., Velsko, C.A., Moran, J.E., Esser, B.K., 2013. A Membrane Inlet Mass Spectrometer for Noble Gases at Natural Abundances in Gas and Water Samples, *in press*, Rapid Communications in Mass Spectrometry.

- **NG-MIMS for groundwater studies is an active field in Europe and to a lesser extent in this country**
  - **Similar but not identical instrument from Europe:** Mächler, L., Brennwald, M.S., Kipfer, R., 2012. Membrane Inlet Mass Spectrometer for the Quasi-Continuous On-Site Analysis of Dissolved Gases in Groundwater. Environmental Science & Technology 46, 8288-8296.
  - **A MIMS, but not capable of measuring xenon:** Kana, T.M., Darkangelo, C., Hunt, M.D., Oldham, J.B., Bennett, G.E., Cornwell, J.C., 1994. Membrane inlet mass spectrometer for rapid high precision determination of N2, O2, and Ar in environmental water samples. Analytical Chemistry 66, 4166-4170.

Age tracers for longer travel times (2-60 years):
Nitrate is the most important water quality issue in California groundwater and requires age dating on a decadal time scale

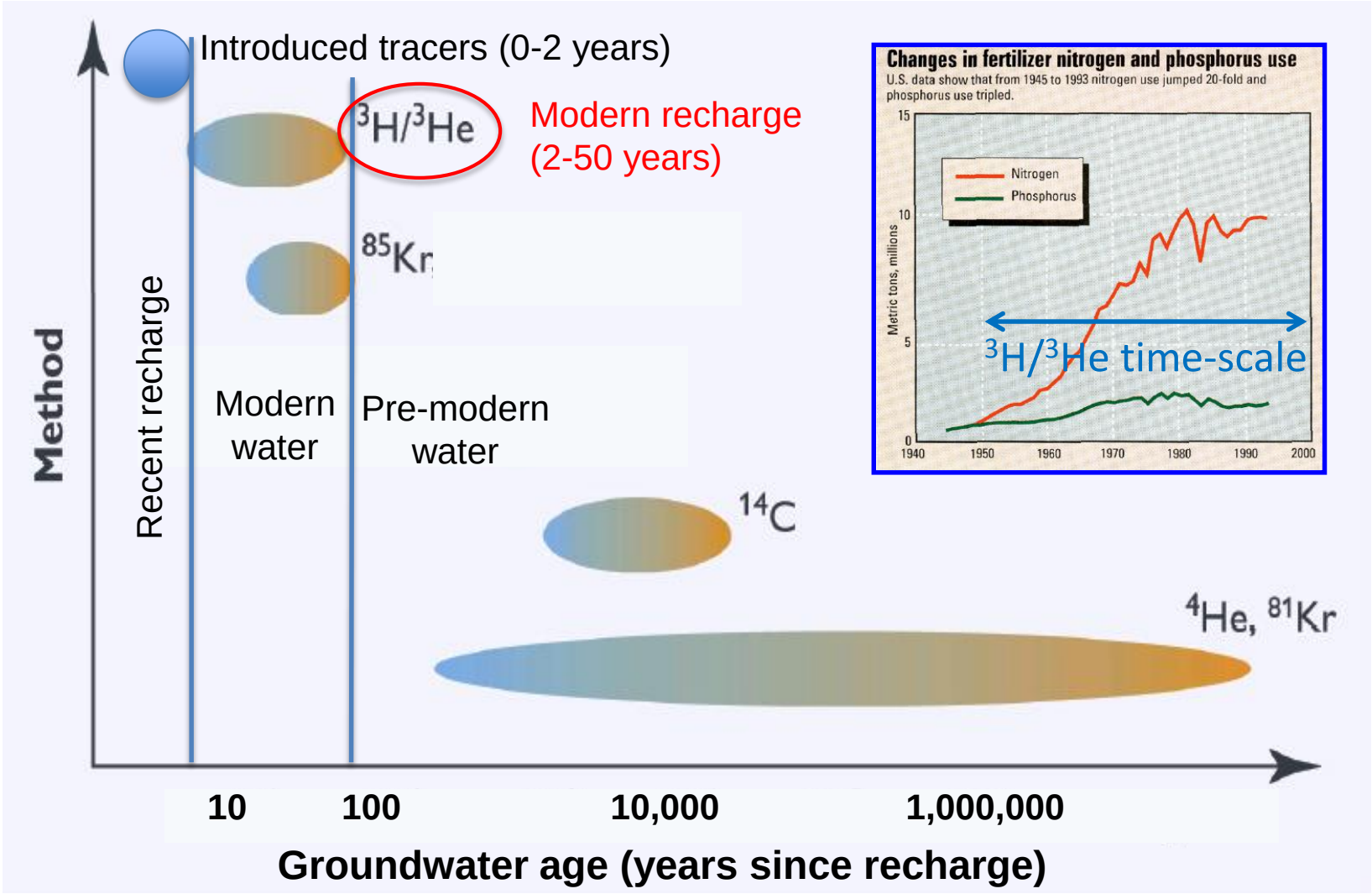




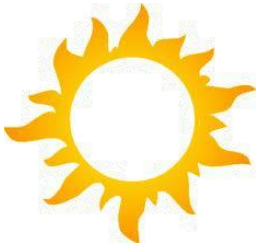
Most public-drinking water wells in California produce water with measurable tritium.

Groundwater monitoring for contaminant source attribution, vulnerability assessment, and basin characterization requires tracing groundwater on a 0-60 year time scale

GAMA Special Studies is developing new tracers to trace recent recharge

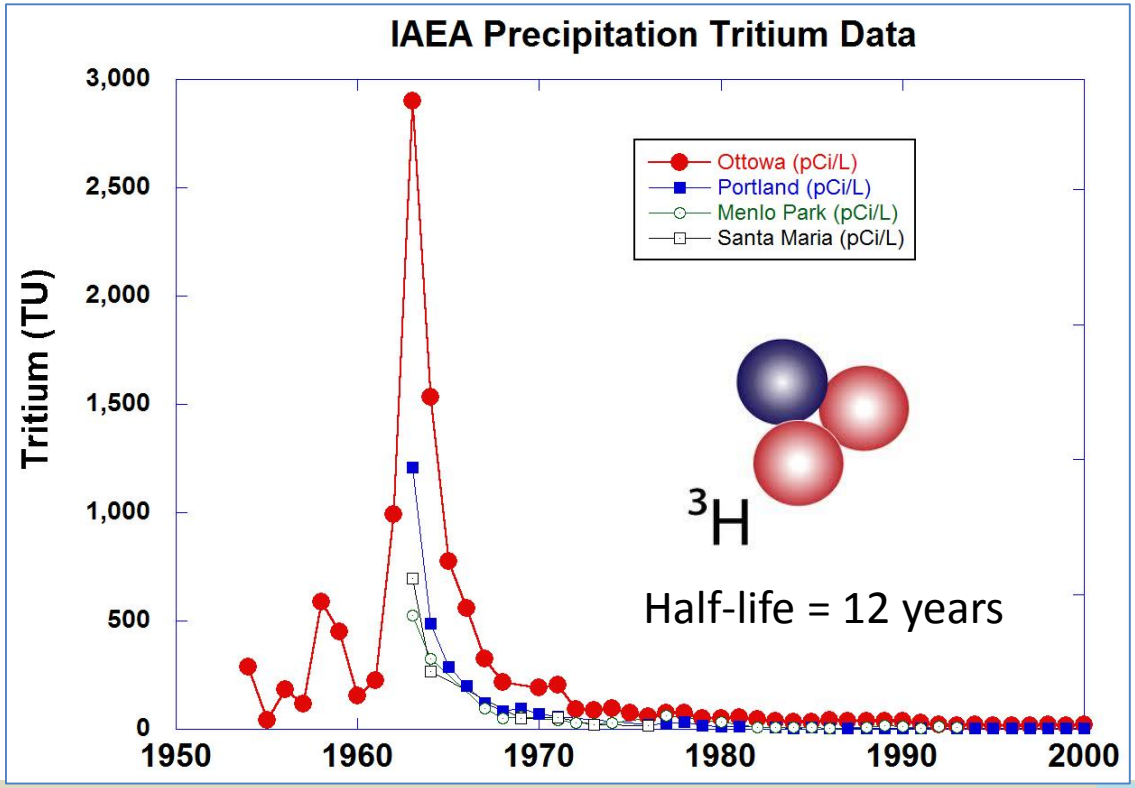


Tritium and its decay product ^3He are used to determine groundwater age (<50y)



Cosmic rays

Atmospheric weapons testing



HTO

Groundwater recharge

Tritium DL < 1 pCi/L

Rainfall today = ~10 pCi/L

Tritium MCL = 20,000 pCi/L

Why not just use tritium alone?

Tritium activity is affected by groundwater age, groundwater mixing *and recharge source*

Location	Tritium (pCi/L)	GW age (years)
Bakersfield	11.1	15
	11.3	34
San Jose	12.4	11
	12.5	42

Irrigation with pumped groundwater

- **Will not affect** tritium-helium groundwater ages
- **Will affect** tritium-only model ages

The use of the tritium/helium-3 method also gives valuable information on

- **Recharge Temperature and Elevation:** *Pond vs river; high vs low elevation*
- **Pre-modern recharge:** *Mixing between water older than and younger than 50 years*
- **Very old water components**: *Helium-4 age dating*
- **Excess air and style of recharge:** *Injection vs surface spreading*

Tritium/helium-3 groundwater age dating and noble gas geochemistry is a signature LLNL capability

- **LLNL is one of two high-throughput noble gas mass spectrometry labs in the country**
  - 500-1,000 samples per year
  - ^{3}He accumulation for ^{3}H determination
  - Noble gas composition by isotope dilution on a residual gas analyzer
  - $^{3}He/^{4}He$ on VG5400

One of two 12-position sample manifolds under LabView control

Ate Visser, lab manager

Noble Gas Mass Spectrometry

The minimum detection level for ^{3}He is about 1 zeptomole (600 atoms). We routinely measure 10^{5} atoms of ^{3}He with accuracy of a few percent

Over the past 15 years, LLNL has made groundwater age-dating accessible to water resource managers

NG-MIMS (Introduced xenon tracer analysis): Opportunities

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  - LLNL does all sample processing, analysis and data reduction
  - LLNL provides guidance on dosing and sampling
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- **Contract with LLNL directly or indirectly**
  - Work with an analytical service provider that contracts with LLNL:
    - *Standard contract quickly put in place*
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  - Contract directly with LLNL:
    - *Non-standard contract, lengthier process*
    - *Act as an analytical services provider of this capability to the California water resource community*

NGMS (Tritium/Helium-3 Age Dating): Opportunities

- **For analytical service providers**
  - **Model 1: LLNL does all analysis**
    - Service provider directly contracts with LLNL, and bundles smaller contracts
    - LLNL analyzes tritium samples and noble gas samples
  - **Model 2: LLNL does noble gas analysis**
    - LLNL analyzes noble gas samples only
    - Service provider analyzes tritium samples by enrichment and liquid scintillation counting
  - **Model 3: LLNL does mass spectrometry**
    - Service provider degasses tritium samples;
    - LLNL analyzes degassed tritium samples, and analyzes noble gas samples

Stretch goal: Develop a small instrument that can measure helium isotopic composition with 2% precision to allow commercial labs to provide tritium/helium-3 groundwater age dates

Degassing rack

NGMS (Tritium/Helium-3 Age Dating): Intellectual Property

- **LLNL does not have ROIs, patents or intellectual property in NGMS**
  - for determination of tritium by helium-3 accumulation, or
  - for determination of helium isotopic composition or noble gas abundance

- **LLNL offers a unique capability: High-throughput analysis of groundwater for tritium/helium groundwater age dating**
  - Past experience has shown that this is difficult to setup and maintain
    - Two high-throughput laboratories in US: LLNL and Columbia University
    - A few low-throughput university laboratories, e.g. University of Utah
  - LLNL must not compete with private industry

- **LLNL does have standard operating protocols for these analyses**
  - Visser, A., Hillegonds, D., Esser, B.K., 2013. Collection and Analysis of Groundwater for Determination of Tritium by Helium-3 Accumulation (SOP-NGMS-121 revision 5). Lawrence Livermore National Laboratory NGMS Standard Operating Procedure (LLNL-TM-623415), p. 9.
  - Visser, A., Hillegonds, D., Esser, B.K., 2013. Collection and Analysis of Groundwater for Determination of Noble Gas Abundance and Helium Isotopic Composition (SOP-NGMS-122 revision 4). Lawrence Livermore National Laboratory NGMS Standard Operating Procedure (LLNL-TM-623335), p. 15.

Age-Dating Groundwater: Opportunities to Work with LLNL

- **INTRODUCED NOBLE GAS TRACERS:**
  Groundwater age dating for young water (0-2 years) using an added tracer.
  - *Application*: Recycled wastewater reuse; Managed aquifer recharge
  - *Opportunity*: Commercialize LLNL NG-MIMS

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  Groundwater age dating for older water (2-50 years) using intrinsic tracers
  - *Application:* Contaminant attribution; Groundwater monitoring; Basin characterization
  - *Opportunity*: Make method more available to California water community

- **IF YOU ARE INTERESTED**
  - ***Brad Esser:*** *925-422,-5247, bkesser@llnl.gov*
    https://www-pls.llnl.gov/?url=about_pls-scientific_staff-esser_b
  - ***Aaron Tremaine:*** *925-422-1284, tremaine1@llnl.gov*
  - **State Water Board Reports Library: GAMA Special Studies**
    http://www.waterboards.ca.gov/water_issues/programs/gama/report_depot.shtml

Time for questions and a break